

# Is $\text{Li}_2\text{Pd}_3\text{B}$ a self-doped hole superconductor ?

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We propose that the electrons responsible for superconductivity in  $\text{Li}_2\text{Pd}_3\text{B}$  come from the palladium 4d-electrons. So, its electronic properties are likely to be dominated by strong electronic correlations. The basic unit in this material are  $\text{Pd}_6\text{B}$  octahedra which share vertices to form a 3-dimensional network. Due to the highly distorted nature of the  $\text{Pd}_6\text{B}$  octahedron, one far stretched Pd atom per octahedra becomes almost inactive for electronic conduction. Thus, the material escapes the fate of becoming a half-filled insulating Mott antiferromagnet by hiding extra charges at these inactive Pd sites and becomes a self-doped correlated metal. We propose a 3-dimensional single band t-J model which could be the correct minimal model for this material.

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Recent discovery of 8 K superconductivity in a non-oxide material  $\text{Li}_2\text{Pd}_3\text{B}$  [1], has once again opened up challenges for search of newer superconductors. This is the first observation of superconductivity in metal rich ternary borides containing alkaline metal and Pd ( Pt group), a 4d transition metal.

First metal boride to show superconductivity ( $T_c=4$  K) was  $\text{TaB}_2$ , discovered by Kiessling [3]. Since then many binary and ternary superconducting borides involving 3d transition and rare earth metals were discovered. For a complete bibliography see [4].

$T_c$  remained below 12 K before the discovery of  $\text{MgB}_2$  ( $T_c=39$  K) by Nagamatsu *et al.*, [5]. It still remains a surprise that how such high  $T_c$  in this material can be obtained, even though the present view is that,  $\text{MgB}_2$  is a phonon mediated strong coupling superconductor.

For  $\text{Li}_2\text{Pd}_3\text{B}$  compound, transport and spectroscopic properties are still unexplored, even though the detail structural data is available [6].

In this short communication, we propose that the electrons responsible for superconductivity in  $\text{Li}_2\text{Pd}_3\text{B}$  comes from the palladium 4d-electrons. So, its electronic properties are likely to be dominated by strong electronic correlations. The basic unit in this material are  $\text{Pd}_6\text{B}$  octahedra which share vertices to form a 3-dimensional network. Due to the highly distorted nature of the  $\text{Pd}_6\text{B}$  octahedron, one far stretched Pd atom/octahedra becomes inactive for electronic conduction. Thus, *the material escapes the fate of becoming a half-filled insulating Mott antiferromagnet by hiding extra charges at these inactive Pd sites and becomes a self-doped correlated metal. This is a classic example of Mott insulator doping itself at the cost of elastic energy by deforming the octahedral cages.* We propose a 3-dimensional single band t-J model which could be the correct minimal model for this material.

The structure of  $\text{Li}_2\text{Pd}_3\text{B}$  is cubic having the space group  $\text{P4}_332$ . This is similar to  $\text{Li}_2\text{Pt}_3\text{B}$ . The characteristic building blocks are distorted  $\text{Pd}_6\text{B}$  octahedra,

centered by boron atom. This is similar to metal oxide superconductors, such as, high  $T_c$  oxides, barium bismuthates, strontium ruthenates and sodium cobaltates etc.. The difference being, in oxide superconductors, metal atoms are enclosed by oxygen octahedral cage, whereas in the present material, boron is octahedrally coordinated by Pd metal ions. The Pd octahedra share vertices and form a 3-dimensional network. Lithium partial structure is also interesting. Every Li atom has 3 neighbouring Li atoms at a distance of 2.55 Å. Li-Li distance in Li metal is about 3.05 Å. Since Li-Li distance in this material is about 16% smaller compared to lithium metal, one can assume that there is complete transfer of electrons from lithium to Pd-B complex. There are no close contacts between lithium and boron atoms.

As every palladium atom forms the common vertex of two  $\text{Pd}_6$  octahedra, there are eight neighbouring Pd atoms. Out of four Pd atoms in the basal plane above, one is pulled too far out, so that the four Pd-Pd distances are  $2 \times 2.78$  Å, 2.95 Å, 3.52 Å. Similar stretching occurs in the basal plane below also. The stretched Pd atoms in the planes below and above are in different directions (See Fig. 1). Ultimately, one has four short Pd-Pd distance (2.78 Å), two medium bonds (2.95 Å) and two very long bonds (3.52 Å). The short and the medium Pd-Pd bonds (total six in number) are slightly larger than metallic palladium, but the long one is too large for binding interaction (Fig. 1).

Boron is the group 13 element in the periodic table with atomic number 5. Its electronic configuration is  $1s^2$ ,  $2s^2$ ,  $2p^1$ . This means, it can easily accept electrons from the d-shell when it tries to form complexes with other elements such as Pd, Pt etc.. It is also known from the elementary chemistry that boron has the property of distorting a structure whenever it forms metal complexes, hydrides etc. That is the reason why one observes a varieties of structures in boron based materials [7].

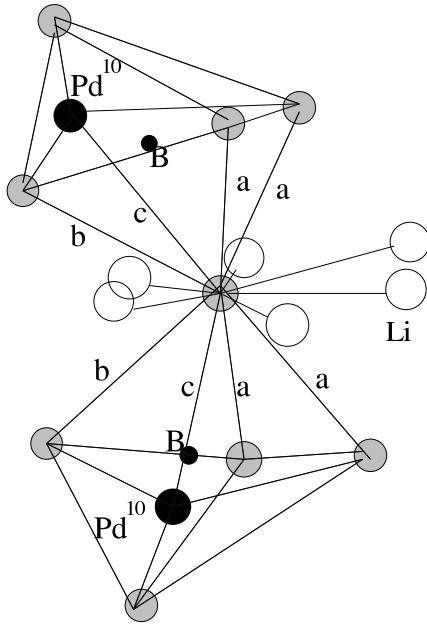


FIG. 1. Two vertex shared  $\text{Pd}_6\text{B}$  octahedra where Pd-Pd bond length ‘c’ is the largest as compared to ‘a’ and ‘b’. The inactive Pd atoms which don’t take part in electronic activities are shown as dark large circles. Also the Boron (dark small circles) and Lithium (large open circles) atoms are shown.

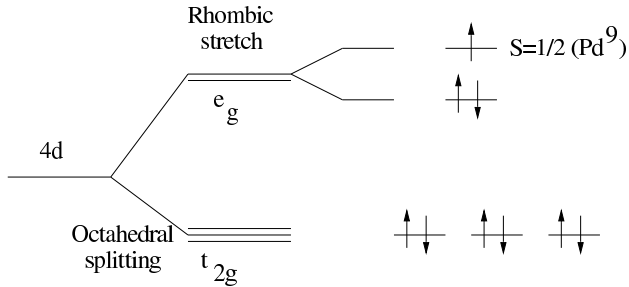


FIG. 2. Crystal-field split of Pd 4d levels.

From nominal valence counting in  $\text{Li}_2\text{Pd}_3\text{B}$ , boron will be in (-5) valence state to make a closed  $2p^6$  configuration. Since lithium is in (+1) valence state, the average Pd valency becomes +1 ( $4d^9$ ), which implies, one electron/hole per Pd atom. Since the material has a 3-dimensional cubic perovskite structure, the 4d level splits into  $t_{2g}$  and  $e_g$  levels due to octahedral coordination, out of which  $t_{2g}$  will be completely filled (see Fig. 2). Due to unusual rhombic stretch of the octahedra, Pd acquires a very low site symmetry. This makes  $e_g$  levels to split further and out of remaining 3 electrons, 2 occupy the lower level leaving the last one in the topmost  $e_g$  level. This gives rise to one electron/Pd site, i.e., a half-filled non-degenerate single band situation. It should be noted that the  $\text{Pd}_6\text{B}$  octahedra with rhombic stretch has escaped the important effects such as Jahn-Teller distortion, Hund coupling and possible high spin ground state

of Pd ions which would have worked against superconductivity. At this stage, a comparison with another non-oxide superconductor  $\text{MgNi}_3\text{C}$  is called for since it has close structural similarity.

$\text{MgNi}_3\text{C}$  has a very symmetrical cubic perovskite structure at high temperature [8] with vertex sharing nickel octahedra enclosing carbon. This is symmetric in all 3 directions, giving rise to isotropic hopping integral in a tight binding sense. The band width estimated from density functional theory [9] is about 2.5 eV, i.e., hopping ‘t’ is about 0.2 eV. We believe that the hopping integral for the present material will be even smaller than that of  $\text{MgNi}_3\text{C}$ , since the structure here is badly distorted. The most important difference in  $\text{Li}_2\text{Pd}_3\text{B}$  as compared to  $\text{MgNi}_3\text{C}$  is one far stretched (*lone*) Pd site/octahedra due to distortion. The hopping matrix element connecting this *lone* Pd site to the other ones will be vanishingly small. This will make the rest of the conducting Pd backbone look effectively very different than the original network of octahedra, but would still form a 3-dimensional network due to large coordination number of Pd atoms. Moreover, due to the 4d character of the carriers, the local Coulomb correlation (U) in this material is expected to be large, similar to that of  $\text{MgNi}_3\text{C}$ , i.e.,  $\sim 4$  eV. Thus, in the limit of strong local Coulomb correlation, one has a Mott insulator and the correct modeling will be a spin-half Heisenberg antiferromagnet on a 3-dimensional lattice. As in other transition metal oxides with a strong Hubbard repulsion, it will lead to the usual superexchange integral between two Pd ions, but since the paths here are not  $180^\circ$ , the antiferromagnetic coupling will be reduced in strength. Considering the above parameters for ‘t’ as well as ‘U’, we estimate the value of J to be  $\sim 50$  meV, i.e., nearly 500 K. Magnetic susceptibility measurement along with a careful tight binding analysis will be able to confirm these estimates.

The *lone* Pd site (one per octahedra), will retain its closed shell electronic configuration  $4d^{10}$  and won’t interact with the rest of Pd d-electron spins. As already been mentioned earlier, due to the inactive nature of the *lone* Pd atom in the octahedra, the average occupancy will not be 9.0 as one would have naively expected. Since the *lone* Pd site/octahedra ( $\frac{1}{6}$ -th of the total palladium sites) holds back the electronic configuration  $4d^{10}$  (atomic), the rest  $\frac{5}{6}$ -th of the palladium atoms will have average occupancy of 8.8 electrons/Pd site, i.e., 20% hole doping. Thus, it becomes a self-doped system over a Mott antiferromagnetic insulating background on a left-over 3-dimensional lattice (where the average Pd-Pd coordination number becomes 7 instead of 8 if it would have been undistorted  $\text{Pd}_6\text{B}$  octahedra). For such a situation, the minimal model would be a 3-dimensional single band t-J model. This can be contrasted with the earlier proposal of self-doping due to externally applied pressure/chemical pressure in transition metal oxide superconductors, fullerenes as well as in organics [10]. In

the present case, *self-doping is done self-consistently by the system itself at the cost of a peculiar distortion of the Pd octahedra.*

Since, our modeling indicates that the carriers in Li-Pd-B ternary borides are holes, one would expect a positive sign in Hall as well as thermopower measurements at low temperature (above  $T_c$ ) which can be tested experimentally.

The next question is then, why would it need such a large (20% doping) carrier concentration to metallize and ultimately give rise to superconductivity? The answer would be the following: If the *lone* Pd atoms would have taken part in the electronic activity, then one would have a perfect 3-dimensional Heisenberg antiferromagnet with possible long range order. In order to destroy a 3-dimensional antiferromagnetic long range ordering and to metallize it (as compared to usual 2-dimensional systems), one would need to go for much higher doping. This dimensional argument might be the reason why one needs more doping for this material than that of standard 2-dimensional (optimal hole doping in cuprate superconductors is about 15%) materials.

However, it should be noted that in the process of making one Pd atom/octahedra electronically inactive, the system loses some of its elastic energy due to lattice distortion but gains electronic energy due to carrier delocalization. Since one observes superconductivity in the system, it implies that the electronic energy wins over the elastic energy.

Much of the experimental data on Li-Pd-B ternary superconductor is unknown. The resistivity at 100 K, on the other hand, is too high compared to other metallic borides superconductors like  $\text{MgB}_2$  ( $\rho \approx 5 \mu\Omega \text{ cm}$ ) [11], but it compares well with other strongly correlated metallic superconductors like, layered cuprates, barium bismuthates, sodium cobaltates etc. (where  $\rho \approx 100 \mu\Omega \text{ cm}$  at  $T = 100 \text{ K}$  is typical [12]). For comparison, an almost isostructural compound like  $\text{MgNi}_3\text{C}$  has  $\rho(T=10 \text{ K}) = 125 \mu\Omega \text{ cm}$  and  $\rho(T=300 \text{ K}) = 325 \mu\Omega \text{ cm}$  [13]. For  $\text{Li}_2\text{Pd}_3\text{B}$  [14],  $\rho(T=10 \text{ K}) = 70 \mu\Omega \text{ cm}$  and  $\rho(T=300 \text{ K}) = 120 \mu\Omega \text{ cm}$ . In case of  $\text{MgNi}_3\text{C}$ , resistivity is linear in temperature upto 60 K as well as for  $T > 60 \text{ K}$  (up to 300 K) with a break of slope at  $T=60 \text{ K}$  [13]. Similar change of slope in resistivity at 60 K has been observed for  $\text{Li}_2\text{Pd}_3\text{B}$  [14]. The overall T-dependence of resistivity in this material is almost identical to that of  $\text{MgNi}_3\text{C}$ . The fall in resistivity at  $T=50$  to 60 K suggests a pseudogap physics (reduction in density of states). Similarity with the physics of superexchange dominated strongly correlated metals such as high  $T_c$  oxide is obvious.

From the resistivity of  $\rho = 120 \mu\Omega \text{ cm}$  at  $T=300 \text{ K}$ , we estimate the mean free path to be about 200 Å, i.e., 30 lattice spacing, implying a good metal. One difference with cuprates is the large residual resistivity,  $\rho \approx 50 \mu\Omega \text{ cm}$ . This is true for  $\text{MgNi}_3\text{C}$  as well. In  $\text{Li}_2\text{Pd}_3\text{B}$ , the *lone* defect Pd sites (non-conducting) might form a back-

ground charge density wave. The additional low energy scattering from the fluctuations of this charge density, would be responsible for such a large residual resistivity. We believe, this could be a generic feature of strongly correlated metals, where various kinds of density waves competes with superconductivity. This clearly indicates that electronic correlations in this material is at work which might be responsible for largely linear T dependence of low temperature resistivity. We believe that such non-Fermi liquid behaviour might continue to occur in many other measurements also.

The basic degrees of freedom and their interactions can be captured by a model hamiltonian which can be written as,

$$H = -t \sum_{\langle i,j \rangle \in \{A\}, \sigma} (C_{i\sigma}^\dagger C_{j\sigma} + h.c.) + J \sum_{\langle i,j \rangle \in \{A\}} \mathbf{S}_i \cdot \mathbf{S}_j - E_I \sum_{j \in \{A\}, \sigma} n_{I\sigma} \mathbf{u}_{\mathbf{j}} + \frac{\lambda}{2} \sum_{i \in \{B\}, j \in \{A\}} \mathbf{u}_{\mathbf{ij}}^2 \quad (1)$$

where, ‘t’ and ‘J’ are the standard hopping and the superexchange integral as has already been mentioned. Here,  $C_{i\sigma}^\dagger$  is the electron creation operator at site ‘i’, with spin projection ‘σ’ and  $\mathbf{S}_i$ , the spin operator of palladium  $4d^9$  active sites.  $\{A\}$  denotes sublattice A for active Pd sites ( $\frac{5}{6}$ -th of total Pd sites) and  $\{B\}$  refers to the rest (inactive *lone* Pd sites).  $E_I$  is the reduction (note the negative sign) in the inactive Pd site energy (I is the inactive Pd site) due to local distortion of the lattice, i.e., whenever  $\sum_j < \mathbf{u}_{\mathbf{ij}} > \neq 0$ ,  $\mathbf{u}_{\mathbf{ij}}$  being the lattice displacement vector between i and j Pd atoms. The last term in the hamiltonian is the increase in the elastic energy cost due to lattice distortion and  $\lambda$ , the elastic constant. The last two terms in the hamiltonian represent the balance between the electronic and the elastic energies.

A standard RVB mean field theory for the above 3-dimensional t-J model will provide a rough estimate for the superconducting transition temperature ( $T_c$ ),  $k_B T_c \approx \frac{W}{2} e^{-\frac{W}{J}}$ . Assuming the bare band width W to be nearly 1.5 eV (It is reduced as compared to  $\text{MgNi}_3\text{C}$  because of the highly distorted nature of the present material), 20% doping makes it even smaller, i.e., 0.3 eV. Considering J to be nearly 50 meV, one obtains  $T_c \approx (1-10) \text{ K}$ , which compares well with the experiment.

Superconductivity in Li-Pd-B ternary boride has been confirmed from magnetization as well as resistivity measurements. Magnetoresistivity measurement [1,2] reveals that the upper critical field  $H_{c2}(0)$  in this material is about 4 T which is well within the Pauli paramagnetic limit. Considering this value of  $H_{c2}(0)$ , one can estimate the coherence length  $\xi(0)$  which turns out to be much larger (few hundred Å) than the standard high  $T_c$  superconductors. It is well known that in  $\text{Sr}_2\text{RuO}_4$  [15], which is a p-wave (triplet) superconductor, even a small disorder giving rise to a residual resistivity of  $1.5 \mu\Omega \text{ cm}$ , is

capable of suppressing superconducting  $T_c$  to zero. The large residual resistivity along with a low  $H_{c2}(0)$  (no Pauli paramagnetic limit for  $H_{c2}(0)$  exists for triplet superconductors), possibly disfavors a triplet pairing and thus, a likely candidate could be a singlet one in this material.

To conclude, we have analyzed the structural data of a recently discovered Li-Pd-B ternary superconductor. From the elementary electron counting combined with the structural data, we arrive at the conclusion that the low temperature electronic properties in this material are dominated by strong electronic correlations. The basic units in this material are highly distorted  $\text{Pd}_6\text{B}$  octahedra, which share vertices to form a 3-dimensional structure. Due to the distorted nature, one far stretched Pd atom/octahedra becomes electronically inactive and hence the material becomes self-doped with 20% holes as the carriers. The 4d nature of the Pd valence electrons are known to have large on-site Coulomb repulsion and the appropriate model would be a 3-dimensional single band t-J model. *This could be the first example of realizing superconductivity in a 3-dimensional t-J model.* Even though most of the transport and spectroscopic properties in this material are yet to be explored, we expect them to exhibit non-Fermi liquid behaviour at low temperature. More experiments are needed to understand the similarities as well as the differences of all the normal state properties of a predominantly 3-dimensional compound like  $\text{Li}_2\text{Pd}_3\text{B}$  and other quasi two dimensional superconductors such as high  $T_c$  oxides, organics, sodium cobaltates etc.. Existence of superconductivity in 2-dimensional t-J model on a square lattice, is no longer doubted [16,17]. The search for superconducting ground states in 3-dimensional t-J model on various kinds of lattices need to be explored.

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